

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
12 April 2001 (12.04.2001)

PCT

(10) International Publication Number  
**WO 01/25365 A1**

(51) International Patent Classification<sup>7</sup>: C09K 3/00, A23L 1/00

(21) International Application Number: PCT/US00/21991

(22) International Filing Date: 2 October 2000 (02.10.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/157,011 1 October 1999 (01.10.1999) US

(71) Applicant and

(72) Inventor: MCARDLE, Blaise, Lee [US/US]; 1702D  
Sladek Road, New Hope, PA 18938 (US).

(74) Agents: ALDAG, Andrew, J. et al.; Epstein, Edell,  
Shapiro & Finnan, LLC, Suite 400, 1901 Research Boul-  
vard, Rockville, MD 20850 (US).

(81) Designated States (*national*): AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: ANTICAKING AND ANTIDUSTING COMPOSITION AND CORRESPONDING METHODS

(57) Abstract: An anticaking and antidusting composition is disclosed that comprises a protein, a saccharide, an alkali metal or alkaline earth metal salt and an acid. The composition is effective in preventing the agglomeration or caking of particulate materials, namely inorganic salts, and can effectively treat such materials utilizing amounts less than 100 ppm by weight of material being treated. Methods of preparing the composition are also disclosed as well as methods for treating a particulate material with the composition.

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## ANTI-CAKING AND ANTI-DUSTING COMPOSITION AND CORRESPONDING METHODS

### CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application claims priority from U.S. Provisional Patent Application Serial No. 60/157,011 entitled "Anticaking and Antidusting Composition", filed October 1, 1999. The disclosure of this provisional application is incorporated herein by reference in its entirety.

### BACKGROUND OF THE INVENTION

#### 10 Field of the Invention

This invention relates to compositions that can be applied onto granules of inorganic salts, particularly granules of sodium chloride, to reduce the tendency to cake on storage and to minimize fugitive dust.

#### 15 Related Prior Art

Many hard crystalline materials, particularly inorganic salts and mineral ores, tend to contain fines or to be friable and form fines, and these fines can be a nuisance. Also, these materials tend to harden and form large, agglomerated masses upon exposure to moisture in humid environments, particularly during long periods of storage. These hardened masses are generally referred to as cakes. Some cake formations become very rigid and resistant to separation, making the material very difficult to transport and to break apart so as to facilitate its use in particular applications. In certain situations where an enormous amount of a material has formed as a solid cake, explosives may be necessary to separate the cake into particulate matter.

20 It is desirable to provide an anticaking agent, in either solid or liquid form, that will be effective when applied to salts in a small amount to minimize dusting and to reduce the caking tendencies for extended periods of time so that the coarse granular crystalline materials will remain easily movable, despite long term storage, and ready for use by the consumer.

25 Economization and automation of industrial processes for inorganic salts require the salt to be in a granular form so that it can flow freely during subsequent processing steps. In emptying storage silos containing tons of inorganic salt, for example, there is increased operational expense and potential danger on account of the tendency of the salt to cake. The salt

5 cakes must be disintegrated by a mechanical auxiliary apparatus in order to be emptied or loaded from the silos. Additionally, during commercial use of the salt, any step of dosing or mixing agglomerated or caked salt together with other substances is difficult due to the extent of the caking.

10 Many attempts have been made to find ways and means to reduce or entirely eliminate the tendency of inorganic salts to harden. One of the best known processes consists of dry mixing with such salts finely divided fillers, such as silica, alkali, alkaline earth and aluminum silicates, aluminum oxide, magnesium oxide, calcium oxide or alkaline earth carbonate. These additives form a loose jacket around the individual salt crystals or granulates that in the recrystallization of the salt prevent a formation of bridges between the individual particles and therefore the potential for caking.

15 The disadvantage of these additives is that they must be used in relatively large amounts in order to produce a suitable anticaking effect. Through the use of large amounts of these additives the products tend to lose most of their clear solubility in water.

20 Organic additives such as oils, glycerine, paraffins, paraffin oils, alkyl sulfonates or fatty amines, are also effective in the prevention of anticaking in organic salts. However, these additives

for the most part are disadvantageous in that they can only be placed on the salt at great industrial expense. For example, a dosing of a hot salt, as it comes out of production, by means of coco-fatty amines is practically impossible because of the odor troubles and danger to health associated therewith. The amines cannot be added during the salt production step, but rather must be added in an additional step after the salt cools. In the interim storage of the salt there is no protection against the possibility of caking.

25 It has long been known that the hardening of alkali chlorides can be reduced by an addition of complex ferrocyanides. These products are expensive and are typically utilized in large amounts based upon the total amount of alkali chloride product being treated. Additionally, the use of ferrocyanides is of some concern due to its potential toxic effect to the environment, e.g. in road salt applications where run-off of treated road salts may wind up in lakes and streams.

5 It is the object of the present invention to provide an effective anticaking and antidusting agent for inorganic salts that is environmentally safe and contains only metals such as alkali metal or alkaline earth metals.

10 It is a further object of the present invention to provide an anticaking and antidusting agent that is highly effective when added in relatively low dosage amounts to inorganic salts in either a powder form or a liquid spray form.

It is yet another object of the invention to provide a modified inorganic salt product containing the anticaking and antidusting agent that is resistant to caking when exposed to high humidity and other moisture conditions.

### 15 SUMMARY OF THE INVENTION

The aforementioned objects are accomplished by providing an agglomeration preventing or anticaking agent for inorganic salts, as well as a process for the production of such agent, wherein the agent comprises a protein, a saccharide, an alkali metal or alkaline earth metal salt and an acid. The anticaking agent of the invention is especially suited for the prevention of caking together and for preserving the flowability of salts, specifically alkali chlorides, e.g. sodium chloride or potassium chloride, and alkali chloride containing salt mixtures. The protein in the agent is preferably a prolamine, most preferably zein. The saccharide is preferably a polysaccharide, most preferably a guar gum. The salt is preferably sodium chloride, most preferably sodium chloride with trace amounts of magnesium chloride and calcium chloride. The acid in the agent is preferably an organic acid, and most preferably at least one of citric acid and ascorbic acid. In a most preferred embodiment of the invention, the anticaking agent composition comprises predominantly guar gum with small amounts of the prolamine, salt and acid.

25 The present invention also relates to a method of making the anticaking agent, comprising mixing a protein, a saccharide and a salt in an aqueous organic solvent that contains an acid until a complex is formed. The resultant complex is then separated from the solvent and dried so as to form the anticaking agent of the invention.

30 The present invention further relates to methods for applying an effective amount of the anticaking agent to an inorganic salt to prevent the modified salt mixture from caking, wherein the application of the anticaking agent to the inorganic salt can be in a solid or liquid form. A

5 modified salt product that contains an effective mixture of the anticaking agent is also encompassed by the invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 In accordance with the present invention, an agglomeration preventing or anticaking agent comprises a complex of a protein, a saccharide, preferably a polysaccharide, an alkali metal or alkaline earth metal salt and an acid, preferably an organic acid. The components of the complex are preferably not toxic and are environmentally friendly, unlike some of the other commercially available anticaking agents (e.g. ferrocyanide compositions).

15 The anticaking agents are also useful in the prevention of dust formation in normally dusty solid materials, namely particulate organic and inorganic material such as wheat, coal fines and the like. It is noted that the agent compositions disclosed in the invention for use as anticaking agents may be applied in the same manner and proportions to various materials to prevent the formation of dust at the surface of those materials.

20 The anticaking agent compositions of this invention may be employed by spraying the agent in liquid form onto coarse granules of salts, particularly sodium chloride or dietetic salt. The typical coarse granules are usually in the range of 1 to 5 millimeters in diameter, usually from 2 to 3 millimeters. The anticaking agents may also be employed by dry blending the agent in powder form into the salt compositions or dissolution into a salt brine prior followed by crystallization of the modified salt from solution.

25 Protein and polysaccharide components utilized in the present invention include a water-soluble monosaccharide or polysaccharide and a substantially water-insoluble protein. Those two components form a complex together when mixed either in granular form or in solution. Mixing those two components in an organic solvent together with the salt and acid utilized in the invention forms a unique complex in solution that is useful as an anticaking agent.

30 Proteins useful in formulating the anti-caking agents include any protein that is predominately or substantially water-insoluble. Vegetable proteins or prolamines are particularly preferable due to their availability and low cost. Prolamines are cereal-derived proteins that are insoluble in water, absolute alcohol or neutral solvents and soluble in dilute (80%) alcohol. Examples of suitable prolamines for use in the present invention include, but are not limited to,  
35 corn-derived prolamine or zein, barley-derived prolamine or hordein, wheat-derived prolamine

5 or gliadin, millet and combinations thereof. In a preferred embodiment of the invention, the vegetable protein or prolamine used in the composition is zein or corn gluten. Corn gluten is obtained from corn or maize. The zein may be physically extracted from the corn gluten or, alternatively, the entire corn gluten may be provided as a mashed paste or powder.

10 Examples of monosaccharides and polysaccharides that can be used to prepare the anticaking agents include, but are not limited to fructose, glucose, lactose, maltose, sucrose, water-soluble cellulose derivatives, seaweed polysaccharides such as alginate and carrageenin, seed mucilaginous polysaccharides, complex plant exudate polysaccharides such as gum Arabic, tragacanth, guar gum, pectin, ghatti and the like, and microbially synthesized polysaccharides such as xanthan gum. In a preferred embodiment, the polysaccharides are guar gum, pectin, gum  
15 Arabic and combinations thereof. The most preferred polysaccharide for use in the present composition is guar gum, which has been found to be effective in binding and stabilizing the components of the agent.

20 The salts utilized in making the anticaking compositions of the invention include alkali and alkaline earth metal salts. Such salts may include chlorides, carbonates, sulphates, silicates and combinations thereof. Particularly useful salts are sodium, magnesium and/or calcium salts, preferably sodium chloride, magnesium chloride and calcium chloride. In a most preferred embodiment, calcium chloride and magnesium chloride are provided in trace amounts within sodium chloride, wherein the weight ratio between the two is about 3:1 of calcium chloride to magnesium chloride. A typical sodium chloride salt utilized in making the anticaking agent of  
25 the invention includes about 0.06% by weight of calcium chloride and 0.02% by weight of magnesium chloride.

30 Any acidic compound is useful in the present invention, including inorganic acids such as carbonic acid, sulfuric acid, hydrochloric acid and the like. However, it is preferable to utilize organic acids, preferably  $C_1$  to  $C_{20}$  organic acids. Suitable organic acids include, but are not limited to, citric acid, malic acid, adipic acid, tannic acid, lactic acid, ascorbic acid, acetic acid, fumaric acid and the like as well as combinations thereof. In a preferred embodiment, citric acid or a combination of citric acid and ascorbic acid is utilized.

35 The anticaking agent is generally prepared by mixing all of the components in an aqueous organic solvent system. A complex comprising the protein, saccharide, salt and acid forms within the upon addition and adequate mixing of the components to the solvent system.

5 Although a complex will form based upon the addition of components in any order, it is preferable to add the acid to the solvent before the protein during the preparation of the anticaking agent of the invention. The acid facilitates adequate dispersion of the protein in the solvent to ensure adequate mixing of the agent components and formation of a complex in solution. In a generally preferred method for preparing the agent, a sufficient amount of soluble  
10 monosaccharide or polysaccharide is first dissolved in an aqueous organic solvent system. A sufficient amount of acid and an alkali or alkaline earth metal salt are then added to the solution, followed by the addition of a sufficient amount of water-insoluble protein or prolamine. Upon addition of the protein and adequate mixing, a complex forms within the solution. If desired, the solvent is then separated or evaporated from the solution to yield the final anticaking agent.

15 The aqueous organic solvent system is a mixture containing at least one organic solvent in water. Suitable organic solvents include, but are not limited to, alcohols such as ethyl alcohol and isopropyl alcohol, glycols such as propylene glycol and polyethylene glycols, and, ketones such as acetone. In a preferred embodiment of the invention, the aqueous organic solvent system is either aqueous ethyl alcohol or aqueous isopropyl alcohol. Alcohols generally are preferred  
20 because they can hold up to six grams of the prolamine in solution for each 100 milliliters of alcohol. The desired ratio of water to organic solvent in the aqueous organic solvent system is dependent on factors such as the miscibility of the solvent in the water and the amount of protein to be dissolved. When the organic solvent system is aqueous ethyl alcohol or aqueous isopropyl alcohol, the amount of water generally ranges between about 10% to 40% by weight and the  
25 amount of alcohol generally ranges between about 60% to 90% by weight. Preferably, the amount of water in such systems is between about 25% to 35% and the amount of alcohol is between about 65% to 75%.

The preferred final composition by weight of the dried anticaking agent is as follows: between about 0.00164 - 99.997% of protein, preferably zein; between about 0.001 - 99.87% of  
30 saccharide, preferably guar gum; between about 0.001 - 99.5% of salt, preferably sodium chloride; and between about 0.001 - 10% of acid, preferably citric acid or citric acid combined with ascorbic acid. An anticaking agent will be effective in the prevention of cake formation in salts utilizing any of the previously disclosed weight ratios for each component. However, a preferred embodiment determined as being highly effective as an anticaking agent has a  
35 composition consisting of about 0.1 - 5% by weight of zein, about 90 - 96% by weight of guar

5 gum, about 1 - 3% by weight of sodium chloride and about 0.5 - 3% by weight of citric acid or citric acid combined with ascorbic acid. Most preferably, the composition of each component by weight is as follows: about 0.5% zein, about 95.4% guar gum, about 2% sodium chloride and about 2.1% citric acid.

10 The monosaccharide or polysaccharide, protein or prolamine, alkali or alkaline earth metal salt and acid are added to the aqueous organic solvent system in appropriate amounts based upon the desired final composition of the agent. Since essentially the entire amount of each component added to the solvent forms a part of the complex in solvent, the amount of each component to add to the solvent can be easily determined based upon the desired final composition. A complex will thus form in the solvent based upon components being added in  
15 any amount necessary to yield a final composition falling within the previously disclosed weight percentage ranges. Typically, the total amount of components added to a solvent is less than or equal to about 500 grams per liter of solvent.

The dissolution of components in the solvent is carried out at a temperature between about 20° C (ambient room temperature) and about 60° C, preferably about 30° C, using  
20 conventional agitation methods to form the slurry solution. Mixing of the components in solution is carried out until a complete uniform mixture is attained. Typically, a mixing period of at least 10-30 minutes is required. Preferably, the components are mixed for several hours to ensure complete formation of the complex. The components in solution are mixed by conventional agitation methods including, but not limited to, manual shaking, mechanical  
25 shaking, magnetic stirring, mechanical stirring or a combination thereof. Such mixing results in the formation of the anticaking complex within the solvent.

Once the anticaking complex in solution has been prepared, the solvent may be separated or evaporated so as to yield a dry composition. Any number of conventional solvent removal techniques may be used including, but not limited to, vacuum drying, centrifugation, evaporation,  
30 freeze drying, air drying, convection oven drying or a combination thereof. The complex is typically dried to a moisture content of no more than about 0.1%. The anticaking composition can be further processed by grinding or milling to a desired mesh particle size for use as a powder and the like.

The application of the anticaking composition of the invention to an inorganic salt can  
35 be accomplished in a variety of ways including, but not limited to, dry mixing the composition



5 with the salt, admixing the composition with a solution such as water and spraying onto the salt, and dissolution of the composition in a brine solution followed by recrystallization of the salt within the brine. In one embodiment, the composition of the present invention may be sprayed onto granular salts while these granules are in motion, e.g., while they are being tumbled or conveyed. The manner of spray application is itself well known and a matter of common  
10 knowledge in the field.

In prior art methods for preventing caking of inorganic salts with compositions such as ferrocyanides or aluminum silicon dioxides, typically amounts of 100 ppm or more of the composition in the salt were required to ensure adequate anticaking properties. The anticaking agent of the invention is added to a particular salt in an effective amount to prevent caking of the  
15 salt when exposed to moisture. The term "effective amount" is defined as any amount of the agent that is effective in preventing caking of a salt treated with such agent. Although such effective amount can be greater than 100 ppm, it has been determined that the agent is equally as effective when utilizing amounts much less than 100 ppm.. In fact, it is preferable in most applications to apply the anticaking agent to a salt in amounts of about 3-5 ppm or less, and best  
20 results are obtained when the agent is applied in that dosage range. This represents an economical treatment that is highly effective and which introduces a minimal adulteration to the treated salt product.

Upon adequate application of the anticaking composition of the invention to an inorganic salt in an effective amount, the resultant salt product is modified such that it resists caking in  
25 environments in which the salt is exposed to moisture. It is believed that the modified salt product is a result of a new crystal formation in the salt resulting from the addition of the anticaking composition of the invention.

The following examples show specific methods of making anticaking agents of the invention, methods of applying those anticaking agents to inorganic salts, and test results  
30 showing the performance of the resultant modified salts when exposed to moisture for a substantial period of time. Although the compositions of anticaking agents in some of the examples vary considerably, each of those anticaking agents was found to be effective in preventing the caking of an inorganic salt after application of a sufficient amount of such agent to such salt.

## EXAMPLE 1

One hundred ml of a 70/30-isopropyl alcohol (IPA)/water mixture was mixed in a gravity flask containing a mixing stirrer at a temperature of 25° C. The alcohol water solution was mixed with 0.1 gram of citric acid and 0.1 gram of 100-screen guar gum (from Precem Pvt. Ltd., Bomba, Maharashtra) and stirred for five minutes. To this solution 10 grams of sodium chloride (containing 0.06% by weight of  $\text{CaCl}_2$  and 0.02% by weight of  $\text{MgCl}_2$ ) was added and blended for ten minutes at 100 rpm. Subsequently, 1.0 gram of 60% corn gluten was added and blended at 100 rpm for 2 hours and allowed to stand overnight. At the end of 24 hours the flask was opened at the bottom to separate the liquid and the precipitated material from the resulting mixture.

The liquor was then dried in an oven for 24 hours at 50° C, removed, and ground into a 100-screen powder. Seven grams of this powder was mixed with one metric ton of mined NaCl chemical salt and was found to contribute anticaking and antidusting properties that lasted for several months.

## EXAMPLE 2

Example 1 is repeated with the following modifications: the IPA/water solvent was increased to two hundred ml, and 0.2 gram of citric acid was added to 0.2 gram of guar gum. The gluten charge was increased to 26 grams and the NaCl charge was doubled to 20 grams. A similar anticaking result was obtained when added to one metric ton of NaCl.

## EXAMPLE 3

Example 1 is repeated with the following modifications: 0.4 gram the citric acid was added to 0.4 gram of guar gum. The gluten charge was increased to 52 grams and the NaCl charge was doubled to 40 grams. A similar anticaking result was obtained when added to one metric ton of NaCl.

## EXAMPLE 4

One hundred grams of 60% corn gluten were placed in a 1000 ml plastic beaker to which 0.1 gram of 100 screen guar gum (Precem Pvt. Ltd., Bomba, Maharashtra) was added and mixed

5 by hand for ten minutes thereby dispersing the guar gum with the gluten. The contents of the beaker were then sprayed with ten grams of a 70/30-isopropyl alcohol/water solution. The contents of the beaker were then again hand mixed for one minute and set aside for one hour at 25° C.

10 A solution of 100 ml of a 0.05% sodium hydroxide containing one gram of sodium chloride (containing 0.06% by weight of  $\text{CaCl}_2$  and 0.02% by weight of  $\text{MgCl}_2$ ) was prepared and 1.2 grams of the treated gluten were then added to the solution and stirred for twenty-four hours at 100 rpm. The pH of the solution was monitored and an additional 5 grams of the 0.05% solution was added to the mixer at two-hour intervals to maintain a pH of 12. At the end of 24 hours the solution was filtered to remove the extraneous material. One hundred ml of the  
15 solution was then poured into a five hundred ml glass beaker. To the solution 50 grams of sodium chloride was gradually added resulting in a stiff paste. Ten grams of the paste was mixed with 0.1 gram of citric acid dissolved in two grams of water in a glass beaker. The resulting mixture was dried in an oven for 24 hours and ground into a 100 screen white powder.

20 The powder was then tumble mixed with 100 kg of course chemical grade NaCl salt and evaluated for anticaking properties under various moisture conditions. In all cases after three months of evaluation the modified salt product showed effective resistance to caking.

#### EXAMPLE 5

25 An alcohol solution consisting of 700 ml pure IPA and 300 ml de-ionized water was prepared in a 2 L glass vessel. The vessel was placed on a heated surface maintained at a constant temperature of 30° C and the vessel contents blended with a blender at a rate of 300 rpm.

30 To the alcohol solvent was added 3 grams of citric acid. After blending the contents for an additional five minutes, 2.4 grams of powdered zein was added. The mixture was continuously blended until the zein had completely dissolved (about twenty minutes), forming a slurry in the vessel.

35 After complete dissolution of the zein in the solvent, the vessel was removed from the blender and 477 grams of guar gum (Precem Pvt. Ltd., Bomba, Maharashtra) were hand mixed into the solution for ten minutes. Then another 7.6 grams of fine crystal citric acid and 10 grams of fine flaked NaCl were added to the mixture and hand blended. The resultant mixture was

5 allowed to stand and then hand mixed several times over a 24 hour period to assure uniform blending of all of the components.

After 24 hours, the material was spread out into flat pans and allowed to dry for 48 hours at about 50° C. The resultant dried material was then ground to a screen size of 200 and stored in a plastic container.

#### 10 EXAMPLE 6

One liter of 70/30 IPA/water mixture was prepared in a glass beaker. The beaker contents were stirred in a mixer at 200 rpm and heated to a temperature of 30° C. To this mixture was added 1 gram of NaCl, 3 grams of citric acid, and 2 grams of ascorbic acid. After ten minutes of stirring, 25 grams of zein were added and the contents blended for an additional twenty minutes. The solution was then removed from the mixer and allowed to stand for four hours.

15 After four hours, 225 grams of guar gum (Precem Pvt. Ltd., Bomba, Maharashtra) were blended into solution by hand. To this slurry 9 grams of additional NaCl and 255 grams of citric acid were blended. The resulting composition was then placed onto glass trays and dried in an oven at 40° C for 48 hours. At the end of 48 hours, the composition was removed from the glass trays and ground to a consistent size and passed through a 300 screen sieve to form a soft white powder. The powder was stored in a plastic container prior to treating an inorganic salt.

#### 20 EXAMPLE 7

25 One metric ton of clean salt was tumbled with 5 grams of the anticaking composition of Example 5 for five minutes and then dissolved in a brine circuit by live steam in a direct contact heater. The resultant hot slurry was then flash cooled in an evaporator. Upon cooling, the solubility of the slurry was decreased, resulting in crystallization of the salt incorporated with the anticaking composition. The treated salt crystals were then dried to a moisture content of less than about 0.1%. The resultant modified salt product was determined as having effective anticaking properties when exposed to varying moisture levels for months.

#### 30 EXAMPLE 8

Five 5-ton stacks of road grade rock salt were prepared and held in an open field covered by a heavy duty clear plastic sheet. These stacks were exposed to normal seasonal conditions

5 in environments including snow and rain for a period of one year. No attempt was made to protect the salt samples other than covering the salt and protecting it against direct contact with snow or rain. The five stacks consisted of the following:

Stack 1: chemical rock salt containing no additives.

10 Stack 2: chemical rock salt that was spray treated with 5 L of water containing 500 g of a sodium ferrocyanide composition manufactured by Degussa Corporation, Ridgefield Park, NJ.

Stack 3: chemical rock salt that was spray treated with 5 L of water containing 25 g of citric acid and 500 g of the same sodium ferrocyanide utilized in Stack 2.

15 Stack 4: chemical rock salt that was spray treated with 5 L of water containing 25 g of the anticaking composition of Example 5.

Stack 5: chemical rock salt that was spray treated with 5 L of water containing 25 g of the anticaking composition of Example 5 and 25 g of citric acid.

20 After one year of field exposure to the elements, the plastic covers were removed on all of the stacks and the salt in each stack was evaluated for testing. Stack 1 showed severe caking. Stacks 2 and 3 showed moderate caking as well as noticeable shrinkage and yellow discoloration. Stacks 4 and 5 showed relatively no caking, there was no noticeable shrinkage and the color remained white. Any slight caking formed on the surface of stacks 4 and 5 broke apart with the application of finger pressure to the stack surfaces.

25

#### EXAMPLE 9

30 Five grams of the 300 screen anticaking composition of Example 6 were added to a tumbler mixer containing 100 kg of commercially available fine table salt (NaCl). The table salt was blended for five minutes and then packed into 125 g salt shakers for testing. Those shakers were designated Sample A. The modified salt product flowed freely during the packaging. All of the salt shakers utilized in this test had openings which exposed the contained salt to the surrounding environment. The salt shakers were then held for one year under various conditions

5 to test for color, appearance, taste and flowability. The shakers of Sample A were tested with three other samples for caking under humid conditions.

Samples B, C and D were prepared for comparison with Sample A as follows. Sample B consisted of 125 g salt shakers containing the same fine table salt but without any anticaking additive. Sample C consisted of 125 g salt shakers containing the same fine table salt but with an addition of 5 ppm of an aluminum silicon dioxide composition manufactured by J. R. Simplot Company, Boise, ID. Sample D consisted of 125 g salt shakers containing the same fine table salt but with an addition of 0.50% by weight the aluminum silicon dioxide composition.

Twenty-four shakers were taken from each group and immediately tested for caking using the industry standard method of exposure to extreme fluctuations of humidity for a period of 48 hours, followed by drying the salt to a water content of less than 0.1%. After 48 hours, the shakers from each group were analyzed for caking. The Sample B and C shakers showed severe caking, and the Sample C shakers showed moderate caking. The Sample A shakers showed no evidence of caking and had free flowability characteristics.

One hundred shakers from each group were then taken to a test station and exposed to coastal sea humidities ranging from 47% to 78% for a one year period of time. Occasionally during the one year period the shakers from each group were examined for caking, and only shakers from Samples A and D were functional in that the salt could flow from the shaker. Samples A and B retained water and would not decant salt during these field tests. At the conclusion of one year, the samples were dried to less than 0.1% moisture levels and examined for caking. Samples B and C were entirely caked after such exposure during one year, whereas Sample D showed moderate caking. The shakers of Sample A, containing the modified salt treated with the anticaking agent of the invention, showed no signs of caking after the one year exposure at such high humidity levels.

As indicated by the previous examples, the composition of each component in the anticaking agent of the invention may vary significantly without losing the effectiveness of the agent when treating a salt. The examples also indicate that a variety of methods may be utilized to apply the anticaking agent to a salt thereby forming a modified salt product, including mixing of the agent with the salt under both wet and dry conditions. In addition to treating the sodium chloride salts of the examples, the anticaking agent of the invention is also effective in treating

5 other alkali chloride containing industrial salt mixtures, such as potassium chloride and various other fertilizer salts.

10 It should be appreciated that the embodiments in the examples described herein and relating to the manufacture of the anticaking agent of the invention as well as the modified salt product should be considered as illustrative only and should not be taken in a limiting sense. It is believed that other modifications, variations and changes will be suggested to those skilled in the art in view of the teachings set forth herein. It is therefore to be understood that all such variations, modifications and changes are believed to fall within the scope of the present invention as defined by the appended claims.

15

5 In the claims:

1. An anti-caking agent for the prevention of caking of inorganic salts, said agent comprising a protein, a saccharide, a salt comprising an alkali metal or an alkaline earth metal salt, and an acid.

10 2. The agent of claim 1, wherein the protein comprises a prolamine.

3. The agent of claim 2, wherein the prolamine is selected from the group consisting of zein, hordein, gliadin, millet and combinations thereof.

15 4. The agent of claim 3, wherein the prolamine is zein having a weight percentage within the agent in a range of about 0.000164 - 99.997%.

20 5. The agent of claim 1, wherein the saccharide is a polysaccharide selected from the group consisting of guar gum, pectin, gum Arabic and combinations thereof.

6. The agent of claim 5, wherein the saccharide is guar gum having a weight percentage within the agent in the range of about 0.001 - 99.87%.

25 7. The agent of claim 1, wherein the alkali metal or alkaline earth metal salt is selected from the group consisting of chlorides, carbonates, sulphates, silicates and combinations thereof.

30 8. The agent of claim 7, wherein the salt comprises sodium chloride having a weight percentage within the agent in the range of about 0.001 - 99.5%.

35 9. The agent of claim 8, wherein the sodium chloride salt includes calcium chloride and magnesium chloride and the weight ratio of calcium chloride to magnesium chloride is at least 3:1.



- 5           10.    The agent of claim 1, wherein the acid is an organic acid having a weight  
percentage  
within the agent in the range of about 0.001 - 10%.
- 10           11.    The agent of claim 10, wherein the organic acid is at least one of citric acid and  
ascorbic acid.
- 15           12.    The agent of claim 1, wherein the protein is zein, the saccharide is guar gum, the  
salt includes sodium chloride and the acid is one of citric acid and citric acid combined with  
ascorbic acid.
- 20           13.    The agent of claim 1, wherein the protein is zein having a weight percentage in  
the  
range of about 0.001 - 99.997% within the agent, the saccharide is guar gum having a weight  
percentage in the range of about 0.001 - 99.87% within the agent, the salt is sodium chloride  
having a weight percentage in the range of about 0.001 - 99.5% within the agent and the acid is  
one of citric acid and citric acid combined with ascorbic acid, said acid having a weight  
percentage of about 0.001 - 10% within the agent.
- 25           14.    The agent of claim 13, wherein the weight percentage of the protein is in a range  
of about 0.1 - 5%, the weight percentage of the guar gum is about 90 - 96%, the weight  
percentage of the sodium chloride is about 1 - 3% and the weight percentage of the acid is about  
0.5 - 3%.
- 30           15.    A method of manufacturing an anti-caking agent for treating inorganic salts, the  
method comprising  
dissolving a protein in an aqueous organic solvent, said solvent including an acid;  
dissolving a saccharide in the solvent;  
dissolving an inorganic salt in the solvent; and  
mixing the protein, saccharide and inorganic salt in the solvent so as to obtain a uniform  
35   complex comprising the protein, the saccharide, the salt and the acid.

5           16.    The method of claim 15, further comprising separating the uniform complex from the solvent.

10           17.    The method of claim 15, wherein the solvent comprises one of an alcohol, a glycol and a ketone.

18.    The method of claim 15, wherein the solvent is at least one of ethyl alcohol and isopropyl alcohol.

15           19.    The method of claim 18, wherein the acid in the solvent includes an organic acid.

20           20.    The method of claim 19, wherein the organic acid is at least one of citric acid and ascorbic acid.

25           21.    The method of claim 15, wherein the protein is zein, the saccharide is guar gum and the salt is sodium chloride.

22.    A method of treating an inorganic salt, comprising the following steps:  
adding an anti-caking agent to an inorganic salt, wherein the anti-caking agent comprises  
25 a protein, a saccharide, a salt comprising an alkali metal salt or an alkaline earth metal salt and an acid; and  
mixing the anti-caking agent with the inorganic salt so as to disperse the anti-caking agent within the inorganic salt thereby forming a modified salt mixture.

30           23.    The method of claim 22, wherein the anti-caking agent is added to the inorganic salt in an effective amount to prevent caking of the modified salt mixture.

24.    The method of claim 23, wherein the effective amount of anti-caking agent added to the inorganic salt is less than about 100 ppm by weight of the inorganic salt.

5           25.     The method of claim 24, wherein the effective amount of anti-caking agent added to the inorganic salt is in the range of about 3-5 ppm by weight of the inorganic salt.

10           26.     The method of claim 22, wherein the protein is a prolamine selected from the group consisting of zein, hordein, gliadin, millet and combinations thereof, the saccharide is a polysaccharide selected from the group consisting of guar gum, pectin, gum Arabic and combinations thereof, the salt of the anticaking agent is selected from the group consisting of chlorides, carbonates, sulphates, silicates and combinations thereof, and the acid is at least one of citric acid and ascorbic acid.

15           27.     The method of claim 26, wherein the salt of the anticaking agent is sodium chloride.

20           28.     The method of claim 26, wherein the salt of the anticaking agent is sodium chloride mixed with calcium chloride and magnesium chloride.

25           29.     The method of claim 28, wherein the weight ratio of calcium chloride to magnesium chloride in the mixture is at least 3:1.

30           30.     The method of claim 22, wherein the inorganic salt is sodium chloride.

35           31.     The method of claim 22, wherein the anticaking agent is dissolved in water prior to the adding step so as to form an anticaking solution, and the adding step comprises spraying the anticaking solution onto the inorganic salt.

          32.     The method of claim 22, further comprising dissolving the inorganic salt in water prior to the mixing step.

          33.     The method of claim 32, further comprising separating the modified salt mixture from the water by at least one of crystallization of the modified salt mixture and drying the

5 modified salt mixture.

10 34. A modified salt product resistant to caking after exposure to moisture comprising an inorganic salt combined with an anticaking agent, wherein the anticaking agent comprises a protein, a saccharide, a salt comprising an alkali metal salt or an alkaline earth metal salt, and an acid.

35. The salt product of claim 34, wherein the inorganic salt comprises sodium chloride.

15 36. The salt product of claim 34, wherein the protein is a prolamine selected from the group consisting of zein, hordein, gliadin, millet and combinations thereof, the saccharide is a polysaccharide selected from the group consisting of guar gum, pectin, gum Arabic and combinations thereof, and the salt of the anticaking agent is selected from the group consisting of chlorides, carbonates, sulphates, silicates and combinations thereof.

20 37. The salt product of claim 36, wherein the protein is zein, the saccharide is guar gum, the salt of the anticaking agent includes sodium chloride and the acid is at least one of citric acid and ascorbic acid.

25 38. The salt product of claim 36, wherein the salt of the anticaking agent is sodium chloride mixed with calcium chloride and magnesium chloride.

30 39. The salt product of claim 38, wherein the weight ratio of calcium chloride to magnesium chloride in the mixture is at least 3:1.

40. The salt product of claim 34, wherein an effective amount of anticaking agent is present in the salt product to prevent caking of the salt product.

35 41. The salt product of claim 40, wherein the effective amount of anticaking agent present in the salt product by weight is less than about 100 ppm.

5           42.     The salt product of claim 41, wherein the effective amount of anticaking agent present in the salt product by weight is about 3-5 ppm.

          43.     A method of treating particulate material comprising the following steps:  
          adding an agent to a selected quantity of the particulate material, wherein the agent  
10       comprises a protein, a saccharide, a salt comprising an alkali metal salt or an alkaline earth metal salt and an acid; and

          mixing the agent with the selected quantity of particulate material so as to disperse the agent within the particulate material.

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## INTERNATIONAL SEARCH REPORT

 International application No.  
 PCT/US00/21991

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(7) : Please See Extra Sheet. US CL : 252/383,381 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 252/383,381,382,384,385 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched None Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WEST USPAT		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,088,791 A (JONES) 09 May 1978, see the abstract, examples and claims 11-18.	1, 5-8, 10-11, 15-16
X	US 5,665,414 A (SHERWOOD ET AL.) 09 September 1997, see the abstract, and examples.	1-14
X	US 4,330,438 A (DIERASSI ET AL.) 18 May 1982, see abstract, examples, and claims.	1, 5-7, 10-11, 43
X — Y	US 4,183,959 A (WOOD ET AL.) 15 January 1980, see the abstract, and column 3, lines 25-50.	1-14, 34-42, 43 15-21
X	US 4,178,370 A (GLABE ET AL.) 11 December 1979, see the abstract, and examples.	1
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:    *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *A* document defining the general state of the art which is not considered to be of particular relevance    *N* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *E* earlier document published on or after the international filing date    *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *L* document which may throw doubts on priority claims or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed    *F* document member of the same patent family		
Date of the actual completion of the international search 17 DECEMBER 2000		Date of mailing of the international search report 17 JAN 2001
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer JOSEPH D. ANTHONY <i>Joseph D. Anthony</i> Telephone No. (703) 308-0661

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/21991

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,766,330 A (KNIGHTS ET AL.) 16 June 1998, see the abstract, examples, and claims.	1-14, 34-42
Y,E	US 6,126,974 A (ANG) 03 October 2000, see the abstract, examples, and claims.	1-14

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/21991

## A. CLASSIFICATION OF SUBJECT MATTER:

IPC (7):

C09K 3/00; A23L 1/00